

(10)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 188 232
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86100235.0

(51) Int. Cl.⁴: G 03 F 7/02

(22) Date of filing: 09.01.86

(30) Priority: 10.01.85 JP 3070/85

(43) Date of publication of application:
23.07.86 Bulletin 86/30

(84) Designated Contracting States:
DE FR GB

(71) Applicant: Nippon Paint Co., Ltd.
2-1-2, Oyodokita Oyodo-ku
Osaka-shi Osaka-fu(JP)

(72) Inventor: Kanda, Kazunori
2-59-13 Asahigaoka
Yao-shi Osaka-fu(JP)

(72) Inventor: Mizuguchi, Ryuzo
C-410,8 Yawatakitsura
Yawata-shi Kyoto-fu(JP)

(74) Representative: Kinzebach, Werner, Dr.
Patentanwält Reiterstötter, Kinzebach und Partner
Bauerstrasse 22
D-8000 München 40(DE)

(54) Radiation curable liquid resin composition.

(57) A radiation curable liquid resin composition comprising a radiation curable liquid base resin and polymer microparticles having an average particle size from 0.01 to 6 microns. The incorporation of polymer microparticles to the base resin may improve the rheological property of the liquid composition and also the physical properties of cured film therefrom.

EP 0 188 232 A2

The invention relates to a radiation curable liquid resin composition.

BACKGROUND OF THE INVENTION

Liquid resin compositions which cure upon irradiation with high energy radiation have many important advantages.

5 Since they may be cured within a few seconds without heating, they may be applied on thermally deformable substrates and do not require a large equipment upon curing. Since they are usually free from any volatile solvent and utilize electric energy for curing, they do not evolve harmful pollutants to
10 the environment. When they are used as a photosensitive material, a high quality image may be reproduced by using short wavelength radiation. Consequently, they find a wide variety of uses in the coating, electronic, printing and other industry as UV or electron beam curable coating compositions, photoresists, electron beam resists, X-ray resists,
15 printing plate making materials and the like.

As is well-known, these radiation curable compositions are normally liquid prior to curing without using any volatile solvent in order that steps for removing solvent and setting
20 the applied composition may be obviated. However, they have to possess a suitable viscosity level to impart them with desired workability without using such volatile solvent. This prevents prior art radiation curable compositions from being applied in a greater film thickness in a single coating
25 operation. This is because the conventional compositions

tend to run with the increase in the amount applied per unit area. The run property may be improved by the incorporation of fine silica particles or various body pigments. The addition of these inorganic fillers, however, tends to adversely affect the weather resistance, apperance or other physical properties of the resulting film. Besides, these inorganic particles tend to cause absorption or scattering of radiation applied because of the difference in refractive index, particle size distribution and chemical constitution between the inorganic particles and the matrix resin.

This can result in uneven dose of high energy radiation which, in turn, may produce insufficiently cured portions or curing may take place in undesired areas.

BRIEF SUMMARY OF THE INVENTION

It is, therefore, a principal object of the present invention to provide a radiation curable resin composition which can eliminate or ameliorate the above-discussed disadvantages of conventional compositions. Other objects and advantages of the present invention will become apparent to those skilled in the art as the description proceeds.

These and other objects and advantages of the present invention may be accomplished by providing a radiation curable resin composition comprising a radiation curable liquid base resin and polymer microparticles having a particle size from 0.01 to 6 microns.

Examples of high energy radiation include ultraviolet (UV) rays, electron beams, X-rays and other ionizing radiation. UV rays having a wavelength of 100-400 nm, preferably 200-300 nm (known as deep UV rays) may be used. These UV rays possess an energy level as high as 70-300 KCal/mole at which dissociation of molecules of ethylenically unsaturated organic compounds occurs. Therefore, the UV light is capable of producing free radicals and thus initiating addition polymerization of the composition of this invention.

Electron beams, X-rays and other ionizing radiation (including α -, β - and γ -rays and hard X-rays among which β -rays having suitable transmission properties may preferably be used as accelerated electron beams) are capable of producing ions, excited molecules and free radicals to initiate addition polymerization of the composition of this invention.

Preferably, the polymer microparticles consists of internally cross-linked polymers of ethylenically unsaturated polymerizable monomers and are present in the final composition in amounts from 0.1 to 50 %, more preferably from 0.2 to 30 % by weight based on the total solid content thereof.

According to the present invention, the viscosity of the resulting radiation curable resin composition may be controlled to exhibit a yield value by the incorporation of polymer microparticles. In other words, the composition has a high apparent viscosity when stationary but the apparent viscosity decreases sharply when a shear force is exerted.

This enables the composition of this invention to be applied in greater film thickness by a single coating operation without run due to the gravity flow, while retaining a proper workability.

5 The polymer microparticles have chemical constitution and optical properties similar to those of matrix resin and thus they do not adversely affect the transparency and the sensitivity to radiation of the composition of this invention. This avoids insufficient curing or curing of undesired areas
10 from occurring and the appearance of finally cured film is not adversely affected.

 The composition of this invention exhibits improved physical properties such as tensile strength, hardness, adhesion strength, flexural strength, abrasion resistance
15 and the like when compared with the corresponding composition free from the polymer microparticles. This may be explained by a physical interaction between the polymer microparticles and the matrix resin so that stresses are relaxed when applied externally.

20 DETAILED DISCUSSION

 Several methods are known for preparing the polymer microparticles. One method includes the steps of emulsion polymerizing a mixture of ethylenically unsaturated monomers in an aqueous medium, and removing water from the emulsion
25 by means of solvent substitution, azeotropic distillation,

5

centrifugation, drying and the like. Although any conventional emulsifier may be used, amphi-ionic group-containing, water-soluble resins as disclosed in Japanese Laid Open Patent Application No. 58-129066 are preferable. Amphi-ionic group-containing alkyd resins disclosed in U.S. Patent No. 4,322,324 and amphoteric amino sulfonate derivatives of epoxy resins disclosed in U.S. Patent No. 4,379,872 may advantageously be employed.

Another method commonly referred to as the non-aqueous dispersion (NAD) method or precipitation polymerization method comprises polymerizing a mixture of ethylenically unsaturated monomers in a non-aqueous organic liquid such as aliphatic hydrocarbons or solvents having high solubility parameters in which the monomer mixture is soluble but the polymer is insoluble to form a non-aqueous dispersion of the polymeric microparticles.

The average size of polymer microparticles varies with the particular polymerization method. Thus, the emulsion polymerization and NAD methods are suitable for the range of 0.01 to 0.6 micron size, the precipitation polymerization method is suitable for the range of 0.2 to 2 micron size, and the suspension or bulk polymerization methods are suitable for the range of 1 to 6 micron size. The polymeric microparticles used in the present invention may be prepared by any of these known methods.

The starting monomer mixture preferably contains, at least as a portion thereof, a monomer having at least two polymerizable sites per molecule or a combination of two monomers having mutually reactive groups to give micropar-
5 ticles which are internally cross-linked.

The polymeric microparticles of the present invention have a diameter of about 0.01 to 6 microns for retaining a good dispersibility, reactivity and stability in the cross-linkable polymer system.

10 Examples of ethylenically unsaturated comonomers used for the production of microparticles include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, styrene, α -methylstyrene, vinyltoluene, t-butylstyrene,
15 ethylene, propylene, vinyl acetate, vinyl propionate, acrylonitrile, methacrylonitrile, dimethylaminoethyl (meth) acrylate and the like. Two or more comonomers may be combined.

20 Cross-linking comonomers include a monomer having at least two ethylenically unsaturated bonds per molecule and the combination of two different monomers having mutually reactive groups.

Monomers having at least two polymerization sites may typically be represented by esters of a polyhydric
25 alcohol with an ethylenically unsaturated monocarboxylic acid, esters of an ethylenically unsaturated monoalcohol

with a polycarboxylic acid and aromatic compounds having at least two vinyl substituents. Specific examples thereof include ethylene glycol diacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 1,4-butanediol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetracrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, glycerol diacrylate, glycerol allyloxy dimethacrylate, 1,1,1-tris(hydroxymethyl)ethane diacrylate, 1,1,1-tris(hydroxymethyl)ethane triacrylate, 1,1,1-tris(hydroxymethyl)ethane dimethacrylate, 1,1,1-tris(hydroxymethyl)ethane trimethacrylate, 1,1,1-tris(hydroxymethyl)propane diacrylate, 1,1,1-tris(hydroxymethyl)propane triacrylate, 1,1,1-tris(hydroxymethyl)propane dimethacrylate, 1,1,1-tris(hydroxymethyl)propane trimethacrylate, triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, diallyl phthalate, diallyl terephthalate and divinyl benzene.

Combinations of two monomers having mutually reactive groups may be used in place of, or in addition to monomers having two or more polymerization sites. For example, monomers having a glycidyl group such as glycidyl acrylate or methacrylate may be combined with carboxyl group-containing

monomers such as acrylic, methacrylic or crotonic acid. Also, hydroxyl group-containing monomers such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, allyl alcohol or methallyl alcohol may be combined with isocyanato group-containing monomers such as vinyl isocyanate or isopropenyl isocyanate.

Polymer microparticles prepared in an aqueous or non-aqueous medium may be isolated by such conventional means as filtration, spray drying, lyophilization and the like, and used directly or after milling to a suitable particle size. Alternatively, the dispersion containing the microgel particles may be subjected to solvent substitution and the resulting dispersion in a new medium may be incorporated in the composition of this invention.

The particle size distribution of polymer microparticles may be regulated by the selection of polymerization method or by suitably mixing particles having different average particles sizes to achieve optimum rheology control of the composition containing the same. Furthermore, the physico-chemical properties of polymer microparticles such as glass transition temperature, solubility parameter, refractive index may be controlled as desired by suitably selecting their monomeric formulations. Polymer microparticles having on their surfaces functional or unsaturated groups capable of co-reacting with such groups possessed by other polymer microparticles or matrix resin may be incorporated to

enhance the interaction between the polymer microparticles themselves or with the matrix resin. The polymer microparticles may also carry on their surfaces or interior a substance which promotes the radiation polymerization reaction such as photosensitizers or a substance which improves properties of cured composition such as stabilizers.

The proportion of polymer microparticles in the composition of the present invention generally ranges from 0.1 to 50 %, preferably from 0.2 to 30 % by weight of the total solid content of the composition to achieve optimum rheology control and improved physical properties.

A variety of radiation curable liquid resins are known. The base liquid resin to be employed in the present invention may be selected from these known resins depending upon its intended ultimate use. For example, for use as a resist or plate making material, those capable of selectively removing unexposed areas from a base sheet with water, an alkali, an acid or an organic solvent are employed to leave images which have been exposed to high energy radiation.

Typical examples of high energy radiation curable resins are those referred to as photosensitive or photocurable resins. These resins consist of (a) film-forming polymers or oligomers capable (or incapable) of cross-linking through photochemical reactions, (b) photo-polymerizable monomers or low molecular weight oligomers, (c) photo-polymerization initiators or photosensitizers, and (d) heat-polymerization

/o

inhibitors or stabilizers. The resins may optionally contain further ingredients such as photosensitizer enhancers, colorants and other additives as desired.

5 Examples of film-forming polymers or oligomers include unsaturated polyester resins, urethane acrylate resins, epoxy acrylate resins, polyester acrylate resins, spiran acrylate resins and the like.

10 Examples of photo-polymerizable low molecular weight oligomers include low molecular weight oligomers of the above-named film-forming polymers or oligomers. Examples of photo-polymerizable monomers include styrene, vinyltoluene, divinylbenzene, vinyl acetate, (meth)acrylonitrile, esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)-
15 acrylate, glycidyl (meth)acrylate, ethyleneglycol di-(meth)-acrylate and trimethylolpropane tri-(meth)acrylate, diethyl itaconate, dibutyl itaconate, diethyl fumarate, diethyl maleate and the like.

20 Examples of photosensitizers includes benzoin, benzoin methyl ether, benzoin propyl ether, benzoin butyl ether, benzophenone, diacetyl, benzil, dibutyl disulfide, dibenzyl disulfide and the like.

25 Examples of heat-polymerization inhibitors include hydroquinone, t-butylhydroquinone, p-methoxyphenol, catechol, benzoquinone and the like.

//

Other radiation curable resins have similar compositions to the above-discussed photocurable resins except that they do not contain photosensitizers. Since these radiation curable resins are well-known in the art and do not constitute a part of the present invention, further explanation thereon will not be needed to those skilled in the art. The essential feature of the present invention resides in the use of polymer microparticles for controlling rheological properties of known and conventional radiation curable liquid base resins instead of using inorganic microparticles to thereby not only eliminate or ameliorate various disadvantages associated with such inorganic microparticles but also improve physical properties of cured products compared with the corresponding formulations free from such polymer microparticles.

The composition of this invention is therefore particularly useful in a number of its applications, for example, as plate making materials or inks used in the printing industry; as coating compositions, packaging materials or adhesives; as resists, dry films or sealants in processing electronic parts such as shadow masks, printed circuit boards, integrated circuits, LSI circuits and the like; as photoresists used in other fields; as textile treating agents; as photocurable compositions for treating dental caries; and as enzyme immobilizing compositions.

The following examples are intended to illustrate the present invention in further detail. In these examples, all

parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

Preparation of Emulsifier

To a two liter flask having stirring means, a reflux
5 condenser, temperature-control means, a nitrogen gas-intro-
ducing tube and a decanter were added 134 parts of N,N-
bis(hydroxyethyl)taurine, 130 parts of neopentyl glycol, 236
parts of azelaic acid, 186 parts of phthalic anhydride, and
27 parts of xylene. The mixture was refluxed and water was
0 removed as an azeotropic mixture with xylene. The tempera-
ture was raised to 190°C over 2 hours and the reaction was
continued with stirring until an acid number of 145 was
reached.

The reaction product was cooled to 140°C and 314
5 parts of CARDURA E-10 (glycidyl versatate, Shell Chemical
Company) was added dropwise over 30 minutes at 140°C.
The reaction was continued for additional two hours with
stirring. A polyester resin having an acid number of 59,
a hydroxyl number of 90 and a number average molecular weight
0 (\overline{M}_n) of 1054 was obtained.

EXAMPLE 2

Preparation of Emulsifier

A flask used in Example 1 was charged with 73.5 parts
of sodium taurinate, 100 parts of ethylene glycol, and 200
5 parts of ethylene glycol monomethyl ether. The temperature

was raised to 120°C with stirring to give a uniform solution. To the solution was added with stirring a solution of 470 parts of EPIKOTE 1001 (Shell Chemical Company, bisphenol A diglycidyl ether epoxy resin having an epoxy equivalent of 470) in 400 parts of ethylene glycol monomethyl ether over 2 hours. The mixture was stirred at the same temperature for additional 20 hours to complete the reaction. The reaction mixture was treated as in Example 1 above to give 518 parts of modified epoxy resin. The resin had an acid number of 49.4 (KOH titration) and a sulfur content of 2.8% (X-ray fluorometry).

EXAMPLE 3

Preparation of Polymer Microparticles

To a one liter flask equipped with stirring means, cooling means and temperature-control means were added 380 parts of deionized water, 50 parts of the emulsifier resin prepared in Example 1 and 7 parts of dimethylethanolamine. The mixture was stirred at 80°C to make a solution. To the solution was added a solution of 2.5 parts of azobiscyanovaleric acid in 50 parts of water containing 1.6 parts of dimethylethanolamine. Then a monomer mixture consisting of 118 parts of styrene, 118 parts of ethyleneglycol dimethacrylate and 14 parts of 2-hydroxyethyl acrylate was added dropwise over 90 minutes. Stirring was continued for additional 90 minutes to give a polymer microparticle dispersion having a nonvolatile content of 43% and an average

particles size of 45 millimicrons. Polymer microparticles were obtained by lyophilizing the resulting polymer dispersion.

EXAMPLE 4

5 Preparation of Polymer Microparticles

To a one liter flask equipped with stirring means, cooling means and temperature-control means were added 370 parts of deionized water, 40 parts of the emulsifier resin prepared in Example 2 and 3 parts of dimethylethanolamine. 10 The mixture was stirred at 80°C to make a solution. To the solution was added a solution of 4.5 parts of azobiscyanovaleric acid in 45 parts of deionized water containing 4.3 parts of dimethylethanolamine. Then a monomer mixture consisting of 60 parts of styrene, 60 parts of methyl methacrylate, 90 parts of butyl acrylate, 5 parts of 2-hydroxyethyl acrylate and 25 parts of ethyleneglycol dimethacrylate 15 was added dropwise over 60 minutes. After the addition of monomer mixture, a solution of 1.5 parts of azobiscyanovaleric acid in 15 parts of deionized water containing 1.4 20 parts of dimethylethanolamine was added. The mixture was stirred for additional 60 minutes at 80°C to give an aqueous dispersion of polymer microparticles having a nonvolatile content of 39% and a particle size of 50 millimicrons.

EXAMPLE 5

25 Preparation of Polymer Microparticles

A one liter flask equipped with stirring means,

cooling means and temperature-control means was charged with 1000 parts of deionized water, 20 parts of polyvinyl alcohol (average M.W.=1500) and 10 parts of sodium dodecylbenzene-sulfonate. The flask was purged with N₂ gas under stirring at 1000 rpm and the content was heated to 60°C. A mixture of 10 parts of styrene, 30 parts of methyl methacrylate, 10 parts of ethylene glycol dimethacrylate and 1 part of 2,2'-azobis-(2,4-dimethylvaleronitrile) (polymerization initiator sold by Wako Junyaku Co., Ltd., under the trade name of V-65) was added dropwise over one hour. After the addition, the inner temperature was raised to 70°C and the reaction was continued for additional 5 hours under stirring to give a polymer microparticle dispersion. Polymer microparticles were separated from the liquid medium by centrifugating the dispersion and washed with deionized water three times. The average particle size was 5.5 microns.

EXAMPLE 6

Preparation of Polymer Microparticles

A one liter flask equipped with stirring means, cooling means and temperature-control means was charged with 900 parts of isopropyl alcohol and then heated to 50°C while purging with N₂ gas. To the flask was added dropwise a mixture of 10 parts of styrene, 8 parts of methylmethacrylate, 5 parts of n-butyl acrylate, 2 parts of acrylic acid and 25 parts of ethylene glycol diacrylate. Then the mixture was stirred for 10 minutes. After adding 1 part of azobisiso-

butyronitrile, the inner temperature was gradually raised to 70°C and the reaction was continued for 4 hours with stirring. The resulting white precipitate was filtered off, washed with isopropyl alcohol three times and dried in a vacuum oven to give polymer microparticles having a particle size of 1.0 microns.

EXAMPLE 7

Preparation of Polyester Acrylate Oligomer

A flask equipped with stirring means, cooling means and temperature-control means was charged with 134 parts of trimethylolpropane, 462 parts of hexahydrophthalic acid and 30.5 parts of toluene. The mixture was reacted at 150°C for 2 hours. Then 162 parts of butyl acetate and 2 parts of hydroquinone were added to the mixture. A mixture of 426 parts of glycidyl methacrylate, 1 part of hydroquinone, 5 parts of dibutyltin dilaurate and 64 parts of butyl acetate was added dropwise over 5 hours while stirring at 110°C. The reaction was continued at the same temperature for additional 7 hours with stirring to give a resin solution having a solid content of 79% and an \overline{M}_n of 1016. This product is hereinafter referred to as "Resin Composition (A)".

EXAMPLE 8

Preparation of Photosensitive Plate Making Resin Composition

A laboratory kneader was charged with 500 parts of polyvinyl alcohol having a saponification degree of 80.7

mole % and an average M.W. of 500, and 680 parts of deionized water. The mixture was kneaded at 80°C to make a solution and then cooled to 60°C after the dissolution. Then a mixture of 1.2 parts of hydroquinone and 1673 parts of 2-hydroxy-ethyl methacrylate was added dropwise over 30 minutes with stirring. Then the mixture was further mixed with a solution of 50 parts of benzoin methyl ether in 215 parts of DMSO at 60°C for 15 minutes. The resulting product is hereinafter referred to as "Resin Composition (B)".

EXAMPLE 9

High Energy Radiation Curable Liquid Resin

A flask equipped with stirring means, cooling means and temperature-control means was charged with 800 parts of EPIKOTE 1004 (bisphenol A diglycidyl ether epoxy resin sold by Shell Chemical), 200 parts of VERSAMID 230 (polyamide based hardener sold by General Mills), 280 parts of glycidyl methacrylate, 1100 parts of xylene and 1.2 parts of hydroquinone. The contents were thoroughly mixed and then allowed to stand at a temperature of 100-110°C. Then the mixture was allowed to cool to 60°C and xylene was removed under vacuum for 2 hours. To the resulting residue were added 150 parts of methyl methacrylate and 100 parts of butyl acrylate and the mixture stirred for additional 1 hour. The resulting product is hereinafter referred to as "Resin Composition (C)".

EXAMPLE 10

20 parts of polymer particles having an average

particle size of 45 millimicrons prepared in Example 3 were dispersed in 40 parts of isopropyl alcohol placed in a stainless steel beaker. To the beaker were introduced 253 parts of Resin Composition (A) prepared in Example 7 and 4 parts of benzoin methyl ether. Then the mixture was dispersed for 30 minutes by a laboratory disperser to give a photocurable resin composition.

The photocurable resin composition was applied on a clean glass plate to a dry film thickness of 200 microns using a doctor blade, allowed to stand for 2 hours at room temperature and then irradiated with UV light under the conditions set forth below. The resulting cured film was almost transparent and tack-free on finger testing.

A specimen for tensile testing was taken by stripping the film from the glass substrate and tested under the conditions set forth below. The specimen exhibited an initial Young's modulus of 25 kg/mm², an elongation of 41% and a breaking strength of 0.99 kg/mm². The maximum film thickness against run in vertical direction of this composition was 180 microns.

Conditions For Irradiating With UV Light

A high pressure mercury lamp (Nippon Storage Battery Co., Ltd., Model HI-20N, 80 W/cm, equipped with a reflector beam collector) was placed over a conveyer at a height of 80 cm with the orientation of longitudinal axis of the lamp being perpendicular to the moving direction of the conveyer.

The coated sample was passed under the lamp at a speed of 5 m/minutes.

Conditions For Tensile Testing

Using TENSILON tester (Model HI-100, Toyo Baldwin Co., Ltd.), a test was made on a film having a length of 50 mm and a width of 10 mm at a pulling rate of 50 mm/minutes.

COMPARATIVE EXAMPLE 1

The procedure of Example 10 was repeated except that 20 parts of polymer microparticles were replaced with 20 parts of calcium carbonate particles having an average particle size of 40 millimicrons (TM TOYOMAITY, Toyo Denka Co., Ltd.). The resulting cured film was opaque and white and retained some tackiness upon finger testing.

COMPARATIVE EXAMPLE 2

The procedure of Example 10 was repeated except that the polymer microparticles dispersed in isopropyl alcohol were not incorporated. The resulting cured film exhibited an initial Young's modulus of 23 kg/mm², an elongation of 29% and a breaking strength of 0.83 kg/mm². The maximum film thickness against run in vertical direction was 90 microns.

EXAMPLE 11

135 parts of Resin Composition (B) prepared in Example 8 were mixed with 25.6 parts of polymer microparticles prepared in Example 4 in a kneader. The resulting mixture was degassed under vacuum to give a photocurable resin

composition. This composition was heated to 60°C and extruded through a slit die on a tinplate substrate coated with a dispersion of red iron oxide pigment in a polyvinyl alcohol solution. The extrudate was covered by a rigid polyvinyl chloride sheet, pressed for 5 minutes under a pressure of 20 kg/cm² and then dried at 60°C to give a photopolymer plate.

A negative film was placed on the photopolymer plate and the assembly was exposed to light from a mercury lamp for 3 minutes. The exposed plate was then developed by spraying tap water thereon. The resulting printing plate exhibited excellent image reproducibility, a sharp shoulder angle and convex cross-sectional configuration.

COMPARATIVE EXAMPLE 3

The procedure of Example 11 was repeated except that the dispersion of polymer microparticles was replaced with an aqueous dispersion of calcium carbonate (TM TOYOMAITY). The resulting printing plate exhibited poor image reproducibility and a bulged cross-sectional configuration. The reproduced image had a tendency of being expanded.

EXAMPLE 12

100 parts of Resin Composition (C) prepared in Example 9 and 10 parts of polymer microparticles prepared in Example 6 were thoroughly mixed in a disperser and then defoamed to give an electron beam curable composition. This composition was applied on a degreased tinplate to a cured film thickness

of 25 microns using a bar coater. The film was irradiated with electron beam having an electron energy of 300 keV at an electron current of 30 mA until a dose of 3 Mrad was obtained. The resulting cured film was transparent, tack-free and exhibited a pencil hardness of 2H. The adhesion strength according to the cross cut-tape peeling test was 100/100.

COMPARATIVE EXAMPLE 4

The procedure of Example 12 was repeated except that the polymer microparticles were replaced with coated calcium carbonate particles having an average particle size of 0.05 microns (sold by Shiraishi Kogyo Co., Ltd. under the name of HOMOCAL DM).

The resulting cured film was opaque and white.

The film exhibited a pencil hardness of 2H and a cross cut-tape peeling test result of 82/100.

COMPARATIVE EXAMPLE 5

The procedure of Example 12 was repeated except that the polymer microparticles were not incorporated.

The resulting film was transparent and exhibited a pencil hardness of H and a cross cut-tape peeling test result of 98/100.

EXAMPLE 13

100 parts of Resin Composition (A) prepared in Example 7 and 10 parts of polymer microparticles prepared in Example 5 were thoroughly mixed in a beaker using a laboratory

disperser. Then the mixture was defoamed and evaporated under vacuum to remove volatile solvent. An X-ray curable composition was obtained.

5 The composition was applied on a polymethyl methacrylate plate having a thickness of 5 mm to a cured film thickness of 200 microns using a doctor blade. The film was irradiated with X-ray at an acceleration voltage of 50 kV using a tungsten electrode as counter cathode until a dose of 12×10^6 roentgens was reached. The resulting cured film
10 was transparent and exhibited a pencil hardness of H.

COMPARATIVE EXAMPLE 6

The procedure of Example 13 was repeated except that the polymer microparticles were replaced with HOMOCAL DM. The resulting film was opaque and white. The pencil hardness
15 was H.

WE CLAIM:

1. A radiation curable liquid resin composition comprising a radiation curable liquid base resin and polymer microparticles having a particle size from 0.01 to 6 microns.

5 2. The radiation curable liquid resin composition according to Claim 1 wherein said polymer microparticles consist of an internally cross-linked polymer of ethylenically unsaturated polymerizable monomers.

10 3. The radiation curable liquid resin composition according to Claim 2 wherein said polymer particles are present in said composition in an amount from 0.1 to 50 % by weight based on the total solid content thereof.

15 4. The radiation curable liquid resin composition according to Claim 3 wherein said amount is from 0.2 to 30 % by weight based on the total solid content of said composition.

5. The radiation curable liquid resin composition according to Claim 1 wherein said radiation is UV rays.

20 6. The radiation curable liquid resin composition according to Claim 5 further containing a photosensitizer.

7. The radiation curable liquid resin composition according to Claim 1 wherein said radiation is electron beams, X-rays or other ionizing radiation.

8. The radiation curable liquid resin composition according to Claim 1 wherein said base resin comprises a film-forming polymer or oligomer selected from the group consisting of unsaturated polyester resins, urethane acrylate resins, epoxy acrylate resins, polyester acrylate resins and spiran acrylate resins.

9. The radiation curable liquid resin composition according to Claim 8 wherein said base resin comprises an ethylenically unsaturated monomer.

10. The radiation curable liquid resin composition according to Claim 9 wherein said base resin contains a heat-polymerization inhibitor.

11. The radiation curable liquid resin composition according to Claim 2 wherein said polymer microparticles are prepared by emulsion-polymerizing ethylenically unsaturated monomers in an aqueous phase in the presence of an amphoteric group-containing water-soluble resin as an emulsifier.

12 **EUROPEAN PATENT APPLICATION**

21 Application number: **86100235.0**

51 Int. Cl.²: **G 03 F 7/02**

22 Date of filing: **09.01.86**

30 Priority: **10.01.85 JP 3070/85**

43 Date of publication of application:
23.07.86 Bulletin 86/30

86 Date of deferred publication of search report: **03.02.88**

84 Designated Contracting States:
DE FR GB

71 Applicant: **Nippon Paint Co., Ltd.**
2-1-2, Oyodokita Oyodo-ku
Osaka-shi Osaka-fu(JP)

72 Inventor: **Kanda, Kazunori**
2-59-13 Asahigaoka
Yao-shi Osaka-fu(JP)

72 Inventor: **Mizuguchi, Ryuzo**
C-410,8 Yawatakitaura
Yawata-shi Kyoto-fu(JP)

74 Representative: **Kinzebach, Werner, Dr.**
Patentanwälte Reistötter, Kinzebach und Partner
Sternwartstrasse 4 Postfach 86 06 49
D-8000 München 86(DE)

54 **Radiation curable liquid resin composition.**

57 A radiation curable liquid resin composition comprising a radiation curable liquid base resin and polymer microparticles having an average particle size from 0.01 to 6 microns. The incorporation of polymer microparticles to the base resin may improve the rheological property of the liquid composition and also the physical properties of cured film therefrom.



European Patent
Office

EUROPEAN SEARCH REPORT

0188232

Application Number

EP 86 10 0235

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 092 783 (DU PONT) * Whole document *	1-7	G 03 F 7/02
X	EP-A-0 102 830 (MITSUBISHI) * Claims *	1-7	
X	US-A-4 414 278 (A.B. COHEN) * Abstract; column 3, lines 45-49 *	1-7	
X	EP-A-0 041 643 (E.I. DU PONT) * Claims *	1	
X	US-A-3 148 064 (F.J. RAUNER) * Whole document *	1	
A	US-A-4 415 649 (S.H. MUNGER) * Claim 1 *	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			G 03 F 7/02
Place of search THE HAGUE		Date of completion of the search 02-11-1987	Examiner RASSCHAERT A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (03.87) (P0401)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.